Scientific Reviews
&
Chemical Communications

Sci. Revs. Chem. Commun.: 5(1), 2015, 21-28
ISSN 2277-2669

PHOTOCHEMICAL LIGAND EXCHANGE REACTION OF NITROSYL PENTACYANOFERRATE (II) USING THIOUREA

MAYANK R. MEHTA[a], VIPUL P. PRAJAPATI[b] and TARUN PATEL[*,a]

Dept. of Chemistry, PAHER University, UDAIPUR – 313003 (Raj.) INDIA
[a]Dept. of Chemistry, Shri P. H. G. Muni, Arts and Science College, KALOL – 382721 (Guj.) INDIA
[b]Dept. of Chemistry, Sheth M. N. Science College, PATAN – 384265 (Guj.) INDIA

(*Received : 10.12.2014; Accepted : 04.01.2015*)

ABSRACT

Sodium nitroprusside contains cyanide ligand that cannot be so easily replaced chemically. An effort has been made to substitute this ligand by another ligand like thiourea. The progress of this photochemical reaction has been observed spectrophotometrically and the product was isolated and characterized. The effect of different parameters like pH, intensity of light concentration of sodium nitroprusside and ligand concentration on the yield of this substitution reaction has been studied. A tentative mechanism for this reaction has been proposed.

Key words: Sodium nitroprusside, Thiourea, Photochemical substitution reaction.

INTRODUCTION

Aqueous solution of sodium nitroprusside undergoes a complex decomposition process in the presence of light[1]. A number of workers have reported the photosensitivity of aqueous solution of nitroprusside in the nineteenth century, but unfortunately the results reported are contradictory with one another. It may be due to the probable failure to distinguish between primary photochemical reaction and secondary photochemical and/or thermal processes as well as control reaction conditions during irradiation. When aqueous[2] and acidic[3] solutions of the sodium nitroprusside were exposed to diffuse day light, it was reported that nitric oxide wash produced. Prussian blue was precipitated in this solution on long exposure. Mitra et al.[4] reported that initially a reversible reaction takes place on exposure of aqueous solution of $[Fe(CN)_5(NO)]^{2-}$ with UV light. This reaction involves the production of a weak acid. On prolonged irradiation, secondary reaction occurs with the appearance of a dark blue color and the reaction becomes irreversible from pH point of view. The dark blue color was proposed to be due to the formation of some ferrous nitrites. Lal[5] observed that an aqueous solution of $[Fe(CN)_5(NO)]^{2-}$ was converted into $[Fe(CN)_5(H_2O)]^{2-}$ on irradiation in the presence of hydrogen peroxide. A blue product was also reported, when the reaction was carried out in the presence of thiourea[2] and thiocyanate[6]. The blue product was proposed to be $[Fe(CN)_5(H_2O)]^{2-}$. Van Voorst and Hemrnerich[7] investigated the chemical reduction of nitroprusside solution in water and also in N, N-dimethylformamide and reported that the nature of reduced product depends on the acidity of the medium. The products have been tentatively assigned the structures as

---

[*] Author for correspondence; E-mail: maku_mehta@yahoo.in

$[Fe(CN)_5(NO)_3]$ or $[Fe(CN)_5(OH)]^{2-}$. The exchange reaction between $[Fe(CN)_5(NO)]^{2-}$ and CN ions is claimed to be photocatalysed[8]. The cyanide ligand, trans to the NO group was reported to have a preferential exchange[9]. Reactions of thiourea with nitroprusside gave a red colored adduct, which is gradually converted into a blue product[10]. Similar reaction was also shown by aqueous thiocyanate[11]. The formation of a hydroxo complex $[Fe(CN)_5(OH)]^4$, NO_2 and $[Fe(CN)_5(H_2O)]^{3-}$ has been reported by Sahasi[12] in photocatalytic reaction of sodium nitroprusside on some semiconducting oxides. Photochemical generation of nitroprusside induced by MLCT excitation in aqueous solution at room temperature was reported by Song and Lin[13]. The photometric determination of thiourea with the use of sodium nitroprusside was presented by Anisimova et al.[14]

A critical survey of the literature reveals that the photochemistry of sodium nitroprusside has received negligible attention[15]. Ameta et al.[16] have reported the photochemical ligand exchange reactions of sodium nitroprusside by using metabisulphite ions and bicarbonate ions. The photochemical reaction of sodium nitroprusside may be useful to have an insight in the understanding of its photochernical behavior on one hand and it will also provide some alternate routes to prepare some newer complexes on the other. The present work describes the photochernical reaction of pentacyanonitrosyl ferrate (II), $[Fe(CN)_5(NO)]^{2-}$, in the presence of ligand like thiourea.

EXPERIMENTAL

Sodium nitroprusside (EM) and thiourea were used in present investigation. 0.9080 g of sodium nitroprusside and 0.0120 g of thiourea were dissolved in 100 mL doubly water and was exposed to a 200 W tungsten lamp (light intensity = 14.0 $mWcm^{-1}$). The light intensity was measured with the help of a solarimeter (Suryamapi model CEL 201). A water filter was used to cut off thermal radiation. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions.

The progress of the photochemical reaction was observed by taking absorbance at regular time intervals using spectrophotometer (Systronics model no:106). Estimation of Fe and Na in the products were made on atomic absorption spectrometer, AAS (Model Varian Techtron-AA-6D) and the estimation of carbon, hydrogen and nitrogen were made on Carloerba-1106 micro analyzer at Sophisticated Instrumentation Centre For Applied Research & Testing, SICART, Vallabh Vidyanagar, Gujarat.

RESULTS AND DISCUSSION

An aliquot of 5.0 mL was taken out from the reaction mixture and the change in optical density was observed colorimetrically at λ_{max} = 620 nm with time of exposure. It was observed that a plot of log (optical density) v/s time was linear and it followed pseudo-first order kinetics. The rate constant of the reaction has been calculated by the expression.

$$k = 2.303 \text{ x slope}$$

The results are summarized in Table 1 and graphically shown in Fig. 1.

Effect of pH

The photochemical reaction of sodium nitroprusside in presence of thiourea (ligand) may be affected by the pH values and, therefore, the effect of pH on this photochemical reaction has been investigated. The results are reported in Table 2.

Table 1: A typical run

[SNP] = 3.05 x 10^{-2} M
[Thiourea] =1.58 x 10^{-3} M
pH = 4.5
Light intensity = 14.0 mWcm^{-2}
λ_{max} = 620 nm

Time (min.)	O.D.	2 + log O.D.
10.0	0.048	0.6812
20.0	0.102	1.0086
30.0	0.252	1.4014
40.0	0.505	1.7033
50.0	0.788	1.8965
60.0	1.058	2.0245
70.0	1.268	2.1031
80.0	1.345	2.1287
90.0	1.380	2.1399
100.0	1.471	2.1676
110.0	1.589	2.2011
120.0	1.622	2.2101
130.0	1.662	2.2206
140.0	1.705	2.2317
150.0	1.752	2.2435
160.0	1.780	2.2504
170.0	1.828	2.2620
180.0	1.917	2.2826
		k = 1.35 x 10^{-2} min^{-1}

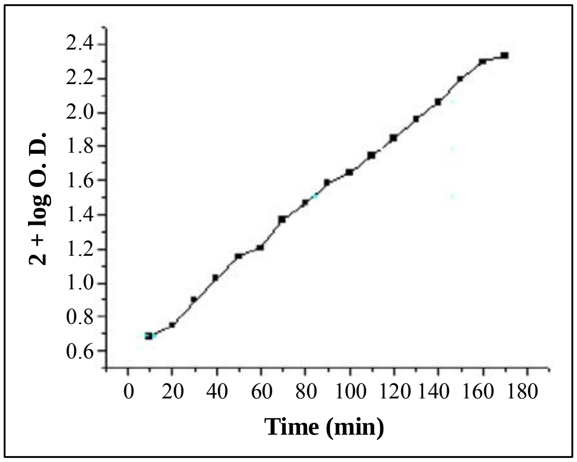

Fig. 1: A typical run

Table 2: Effect of pH

[SNP] = 3.05×10^{-2} M [Thiourea] = 1.58×10^{-3} M

λ_{max} = 620 nm Light intensity = 14.0 $mWcm^{-2}$

pH	**k x 10^2(min^{-1})**
2.0	0.90
2.5	1.04
3.0	1.17
3.5	1.25
4.0	1.31
4.5	**1.35**
5.0	1.27
5.5	1.15
6.0	1.04
7.0	0.89
8.0	0.83
9.0	0.76

It was observed that the yield of this ligand exchange reaction increases on increasing the pH of the reaction medium. It reaches a maximum at pH = 4.5. A decrease in the yield of the product was observed on increasing pH further. It may be explained on the basis that as the pH was increased, the availability of the ligand increases and hence, the reaction rate increases. But, on increasing the pH above 4.5, there is a possibility of a competitive reaction of ligand thiourea, with that of OH^- ions. Thus, a corresponding decrease in the rate of reaction was observed.

Effect of sodium nitroprusside concentration

The effect of the concentration of sodium nitroprusside on the yield of product was observed, by keeping all other factors identical. The range of concentration was kept between 2.04×10^{-2} M to 3.23×10^{-2} M. The results are reported in Table 3.

Table 3: Effect of sodium nitroprusside concentration

[Thiourea] =1.58×10^{-3} M Light intensity = 14.0 $mWcm^{-2}$

pH = 4.5 λ_{max} = 620 nm

[SNP] x 10^2 M	**k x 10^2 (min^{-1})**
2.04	0.74
2.23	0.81
2.38	0.87
2.49	0.90
2.63	1.03

Cont…

$[SNP] \times 10^2$ M	**$k \times 10^2$ (min^{-1})**
2.79	1.14
2.93	1.22
2.99	1.28
3.00	1.30
3.05	**1.35**
3.14	1.26
3.16	1.18
3.18	1.08
3.20	1.00
3.23	0.90

It has been observed that the rate of photochemical reaction of sodium nitroprusside with thiourea increases with an increase in the concentration of sodium nitroprusside. This may be due to the fact that as the concentration of sodium nitroprusside was increased, the number of excited species also increases; thus, resulting into a corresponding increase in the rate of reaction. After a certain limit, if the concentration of sodium nitroprusside was further increased, (i.e. above 3.05×10^{-2} M) there was a decrease in the rate of reaction.

This decrease may be explained on the basis that the substrate is dark red colored, which will absorb a major part of incident radiations travelling through the reaction mixture and, therefore, there will be a decrease in the light intensity reaching sodium nitroprusside in the bulk of reaction mixture. In other words, the solution of nitroprusside will start acting as a filter and as a consequence, the yield was found to decrease.

Effect of thiourea concentration

The effect of concentration of thiourea on the rate of photochemical reaction of sodium nitroprusside was also observed by taking different concentrations of thiourea, keeping all other factors identical. The results are reported in Table-4.

Table 4: Effect of concentration of thiourea

$[SNP] = 3.05 \times 10^{-2}$ M Light intensity = 14.0 $mWcm^{-2}$
pH = 4.5 λ_{max} = 620 nm

$[Thiourea] \times 10^3$ M	**$k \times 10^2$ (min^{-1})**
1.03	0.99
1.10	1.04
1.19	1.07
1.27	1.13
1.30	1.17
1.33	1.26
1.41	1.28
1.50	1.32

Cont…

[Thiourea] x 10^3 M	**k x 10^2 (min^{-1})**
1.58	**1.35**
1.63	1.31
1.70	1.26
1.78	1.23
1.89	1.20
2.00	1.15
2.07	1.13
2.13	1.07
2.19	1.04

It was observed that as the concentration of thiourea was increased, there was a corresponding increase in the rate of reaction, reaching a maximum at [Thiourea] = 3.05 x 10^{-3} M. It can be explained on the basis of the fact that the reaction rate increases due to an increase in the concentration of participating species. On the other hand, a decrease in the rate of reaction was observed on increasing the concentration of thiourea above 3.05 x 10^{-3} M. It may be attributed to the fact that higher concentration of thiourea may hinder its own movement to reach the excited species of sodium nitroprusside in a desired time limit. Thus a decrease in the rate of reaction was observed for higher concentrations of thiourea.

Effect of light intensity

The effect of light intensity on the rate of photochemical reaction of sodium nitroprusside has been observed by varying the distance between the exposed surface of the reaction mixture and the light source. The results are tabulated in Table 5.

Table 5: Effect of light intensity

[SNP] = 3.05 x 10^{-2} M [Thiourea] = 1.58 x 10^{-3} M
pH = 4.5 λ_{max} = 620 nm

Light intensity ($mWcm^{-2}$)	**k x 10^2 (min^{-1})**
6.0	0.94
7.0	1.09
8.0	1.15
9.0	1.22
11.0	1.28
12.0	1.31
13.0	1.33
14.0	**1.35**
15.0	1.35
16.0	1.35
17.0	1.35
18.0	1.35

The results given above indicate that reaction rate is accelerated as the intensity of light was increased. This may be due to the fact that any increase in the light intensity will increase the number of photons striking per unit area of the reaction mixture. After a certain limit (i.e. I = 14.0 $mWcm^{-2}$), no reasonable increase in the rate of reaction has been observed. On using higher intensities of light, rather. It reaches a saturation point at a particular intensity. It suggests that further increase in the light intensity will not increase the rate of this photochemical reaction any more as the surface of the reaction mixture remains fixed. This point was shifted towards lower value when vessels of smaller dimensions were used. A reverse trend was obtained with vessels of larger dimensions.

An effort was made to know the requirement of light in different steps of this reaction. It was observed that the reaction stops at a particular step, as soon as the light source was cut off. The reaction reaches its completion only, when the light exposure was continued throughout the progress of the reaction.

Analysis of the product

The photochemical reaction between sodium nitroprusside and thiourea was carried out. It was observed that the initial light red color of the reaction mixture changes to peacock blue. The reaction was allowed to proceed to completion and then it was filtered. The filtrate was evaporated on a water bath and residue was recrystallised with methanol giving green crystals of the product, which was analyzed as follows:

Elemental analysis

Element	Found%	Calculated%
Fe	19.90	19.86
C	21.30	21.28
N	29.75	29.79
H	1.45	1.42
Na	16.30	16.31
S	11.30	11.35

(i) IR

A comparison of the IR spectra of the sodium nitroprusside, thiourea and the product clearly indicates the removal of nitrosyl ligand from the coordination sphere of the iron. The characteristic bands of NO^+ ligand at 1944 and 670 cm^{-1} were found absent in the IR spectrum of the product.

The solid state IR spectrum of thiourea and the metal complex in the region 4000–400 cm^{-1} were compared and assigned on careful comparison. In the region 3450-3100 cm^{-1}, the N–H vibrations that appear as a broad peak at 3450 cm^{-1} in the spectrum of the ligand, which was shifted to higher wave numbers in the complex. These shifts might be attributed to the S→M bond and C–N bending vibration shows at 1407.08 cm^{-1} in the spectra of the complex. These shifts can be ascribed to increase in the double bond character of the C–N bond on complex formation. The infrared spectrum of the complex confirms that the thiourea ligand was coordinated to the metal ions via the exocyclic sulfur atom with a reduction in the π-electron density of the exocyclic C=S bond. In addition, the $\upsilon_{(C=S)}$ bond of the free ligand is red-shifted to lower frequencies in the complex.

On the basis of the spectral and analytical data, the following tentative structure has been proposed for the compound.

$$Na_2\ [Fe(CN)_4)\ (NH_2\text{-}CS\text{-}NH_2)]$$

In this case, thiourea ion behaves as a bidentate ligand.

Mechanism

On the basis of the experimental observations, a tentative mechanism for the photochemical ligand exchange reaction of sodium nitroprusside has been proposed as

$$Na_2\ [Fe(CN)_5NO] \xrightarrow{h\nu} Na_2\ [Fe(CN)_5NO]^{*}$$

$$Na_2\ [Fe(CN)_5NO]^{*} + H_2O \xrightarrow{h\nu} Na_3\ [Fe(CN)_5(H_2O)] + NO^{+}$$

$$Na_3\ [Fe(CN)_5(H_2O) + NH_2\text{-}CS\text{-}NH_2 \xrightarrow{h\nu} Na_2[Fe(CN)_4(NH_2\text{-}CS\text{-}NH_2)] + H_2O\ + CN^{-}$$

Initially, the sodium nitroprusside is excited by absorbing incident radiations of a desired wavelength. Then its excited state will react with water and as a consequence, water enters the coordination sphere of iron, replacing nitrosylium ion (NO^{+}). This exchange in energetically favorable, because a neutral ligand like water (H_2O), can easily replace a cationic ligand (NO^{+}).

Now, thiourea can easily throw water molecule out of the coordination sphere of iron. Sidewise a bidentate ligand (Thiourea) enters the coordination sphere of iron, replacing two CN^{-} ions. This is evident from the chemical analysis of the product.

REFERENCES

1. J. F. Swinehast, Coord. Chem. Revs., **2**, 385 (1967).
2. O. Baudis, Science, **108**, 443 (1948).
3. E. Justin-Muller, Bull. Soc. Chem., **2**, 1932 (1935).
4. R. P. Mitra, V. S. Jain, A. K. Benerjee and K. V. R. Chari, J. Inorg. Nucl. Cmem., **25**, 1236 (1963).
5. B. B. Lal, Proc. Indian Aced. Sci., **A-14**, 652 (1941).
6. N. Tarugi, Ann. Chim. Appl., **16**, 407 (1926).
7. J. D. W. Van Voorst and P. Hemmerich, J. Chem. Phys., **45**, 3914 (1966).
8. W. Adamson and A. H. Sporer, J. Am. Chem. Soc., **80**, 3865 (1958).
9. J. H. Swinehart and P. A. Rock, Inorg. Chem., **5**, 573 (1966).
10. P. A. Stoire and D. X. West, J. Inorg. Nucl. Chem., **36**, 3883 (1974).
11. J. A. Mecleverty, Chem., Revs., **79**, 53 (1979).
12. S. Sahasi, Ph. D. Thesis, Sukhadiya Uni. Udaipur, India (1991).
13. Q. H. Song and Q. Z. Lin, J. Photochem. Photoboil., **114A**, 181 (1991).
14. L. A. Anisimova, I. A. Yasenko and V. F. Toropova, J. Anal. Chem., **52**, 1049 (1997).
15. P. J. Vyas, Ph.D. Thesis, Sukhadiya Uni. Udaipur, India (2000).
16. S. C. Ameta, P. J. Vyas and P. B. Panjabi, Asian J. Chem., **15**, 279 (2003).